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(54) Adhesive-containing  
microcapsules

(57) An adhesive composition  
comprising an adhesive of the  
chemical reaction or solvent activation  
type is constituted by microcapsules

consisting of at least one of the  
components of the adhesive  
encapsulated within a membrane  
composed of a modified aminoplast,  
the microcapsules being dispersed in  
a medium consisting of the other  
component(s) of the adhesive.

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**SPECIFICATION.****Adhesive containing microcapsules**

The present invention relates to adhesives containing microcapsules. More specifically, the invention relates to adhesives of the chemical reaction type or of the activation-by-solvent type and which contain microcapsules.

Adhesives are classified according to their method of hardening into the following four groups:

**1) Adhesive agent of solvent-evaporation type:**

After applying the agent, all the medium such as a solvent or water originally contained therein disappears from the applied agent by evaporation from the jointed end or absorption to the materials to be adhered, and the thus formed membrane of the adhesive agent exhibits the maximum strength thereof.

**2) Adhesive agent of chemical reaction type:**

A hardened adhesive membrane is formed by a chemical reaction between the resin and the hardener or between the monomer (or oligomer) and the catalyst by mixing two separate components of the adhesive agent, one of which contains the resin or the monomer and the other of which contains the hardener or the catalyst.

**3) Adhesive agent of solvent activation type:**

After painting the adhesive agent on the surface of the body to be adhered and forming a dried membrane of the agent on the surface, a solvent is sprayed thereonto to reactivate the painted surface of the membrane and then the other body to be adhered is placed on the thus reactivated surface of the membrane formed, thereby completing the adhesion.

**4) Adhesive agent of hot melt type:**

After applying the adhesive agent in the molten state thereof onto the surface of the bodies to be adhered, the thus treated bodies are cooled so as to complete the adhesion.

The adhesive agent of chemical reaction type is composed of two mutually separated components which are mixed just before the application thereof and accordingly, such a type of adhesive agent has the demerits of inconvenience in application and of the limitation of the operation time after mixing the two components and of the necessity of discarding the remnant mixture of the two components.

While in the adhesive agent of solvent activation type, there are problems of environmental pollution and in industrial hygiene and safety because of the necessity of using a large amount of an organic solvent.

In order to solve the above-mentioned demerits of some of the conventional adhesive agents, trials of encapsulating a component thereof have been carried out, and microcapsules provided with their membrane made of gelatin or polyamide have been proposed.

However, since the membranous wall of the hitherto proposed microcapsules are generally semipermeable or perforated microscopically, the component of the adhesive agent contained therewithin is apt to be extracted from the microcapsules, and because of the poor resistance of the membranous wall to an organic solvent such as alcohols, ketones and esters, there has been the same kind of demerit of extraction of the content in the microcapsule by such a solvent.

Particularly, in order to use microcapsules in an adhesive agent to which a solvent-resistance is specifically demanded, it is required that (1) the membranous wall of the microcapsule is particularly excellent in solvent-resistance and (2) the microcapsule itself is excellent in pressure-responsiveness to be easily broken by a minute increment of the pressure loaded thereon, and accordingly, it has been very difficult to put such an adhesive agent containing the microcapsules in practical use. Namely, in order to improve the solvent-resistance of the microcapsules to solvents, there have been tried a process of immersing the microcapsules in a basic substance to activate the surface of the microcapsules, a process of bringing the surface into contact with a vapour of an alpha-cyanoacrylate and a process of coating the microcapsules with a substance resistant to the medium for dispersing the microcapsules in the adhesive agent to form the double-layered microcapsules. However, by such a process, the pressure necessary for braking the microcapsules on application becomes too large to use the thus treated microcapsules as the component of the adhesive agent.

An object of the present invention is to provide an adhesive agent containing the microcapsules excellent in solvent-resistance and in pressure-responsiveness, the adhesive agent solving the demerits of the conventional adhesive agents of chemical reaction type and of solvent activation type and being convenient and easy to be handled on application without the necessity of using an excessive amount of components of the adhesive agent.

In the first aspect of the present invention, there is provided an adhesive agent containing microcapsules, comprising said microcapsules consisting essentially of a core substance of at least one of the components constructing said adhesive agent and, as a material for the membrane of said

microcapsule, an aminoplast preliminarily treated by a modifier, and a medium consisting of the other components constructing said adhesive agent, said microcapsules dispersing in said medium and said adhesive agent being the type of chemical reaction or the type of solvent activation.

In the second aspect, there is provided a process for preparing an adhesive agent containing microcapsules, of the type of chemical reaction or the type of solvent activation, comprising dispersing minute liquid particles of at least one of the components of said adhesive agent in an aqueous dispersion of the components for forming an aminoplast, adding an acid catalyst to said aqueous dispersion, thereby bringing the prepolymer of said components for forming said aminoplast into polycondensation, adding a modifier to said aqueous dispersion during or after the completion of said polycondensation, thereby forming said microcapsules encapsulating said at least one of said components within the membrane consisting essentially of said aminoplast modified by said modifier, collecting and drying the thus formed microcapsules, and dispersing said microcapsules in the other components constructing said adhesive agent containing microcapsules.

The characteristic of the present invention is in an adhesive agent containing microcapsules of the type of chemical reaction or the type of solvent activation, said microcapsules consisting essentially of (1) a core substance of one or more than one components of the adhesive agent, which is (are) to be encapsulated within the microcapsule and (2), as a material of the membrane of the microcapsule, an aminoplast treated preliminarily by a modifier in a system consisting essentially of the other components of the adhesive agent.

Namely, the adhesive agent containing the microcapsules, which is the type of chemical reaction or the type of solvent activation according to the present invention takes a form of, in the case where it is the type of chemical reaction, namely, for instance, in the case where the component of the adhesive agent consisting essentially of a resin and a hardener or of a monomer or an oligomer and a catalyst, an adhesive agent containing the microcapsules encapsulating, as a component, the hardener or the catalyst (preferably as small as possible in amount) dispersed in the resin or the monomer and/or the oligomer. In addition, in the case where the component is a multi-component system such as that consisting essentially of the monomer, the catalyst and the hardener, the microcapsules containing the catalyst or both the catalyst and the hardener are dispersed in the monomer in order to prevent the reaction between the catalyst and the monomer, and between the hardener and the monomer.

In this connection, not less than two components which do not mutually react may be separately encapsulated, however, it is preferable to encapsulate not less than two such components simultaneously, and in addition, the catalyst or the hardener may be encapsulated in a dissolved state in a solvent.

On the other hand, the adhesive agent containing microcapsules according to the present invention takes another form of, in the case where it is the type of solvent activation, an adhesive agent containing the microcapsules encapsulating a solvent necessary for dissolving and activating the resin which is to form the adhering membrane dispersed in a solution which contains the resin to be painted on the surface of a material to be adhered (hereinafter referred to as "the resin solution"). Consequently, according to the present invention, since it is necessary to encapsulate the smallest amount of the solvent necessary for activating the resin, the problem of the conventional adhesive agents of the type of solvent activation, caused by the use of a large amount of a solvent, can be solved by this type of adhesive agent.

The important matter in encapsulating at least one of the components of the adhesive agent is that the membranous wall forming the microcapsule is excellent both in solvent-resistance and in pressure-responsiveness.

As a result of the present inventors' studies for obtaining the material for forming a membranous wall of the above-mentioned specificities, it has been found by them that an aminoplast preliminary treated by a modifier is suitable as the above-mentioned material. The "aminoplast" herein mentioned means a resin obtained by bringing at least one prepolymer selected from the group consisting of melamine-formaldehyde prepolymers, urea-formaldehyde prepolymers, melamine-urea-formaldehyde prepolymers, melamine-thiourea-formaldehyde prepolymers and melamine-thiourea-urea-formaldehyde prepolymers or a mixed prepolymer containing a melamine-formaldehyde prepolymer and a thiourea-formaldehyde prepolymer into polycondensation in the presence of both a water-soluble cationic urea resin and an anionic surfactant.

The material for the membrane of the microcapsule according to the present invention comprises an aminoplast prepared by polycondensation in the presence of a modifier.

The microcapsule formed of the thus treated aminoplast is superior in solvent-resistance and free-flowing property to the microcapsule formed of the aminoplast which has not been treated, and in the same time, the microcapsule formed of the thus treated aminoplast exhibits an excellent pressure-responsiveness.

As the modifier used for the above-mentioned object, a phenolic compound such as phenol, resorcinol, catechol, hydroquinone, cresol, xylenol and saligenin and a polyalkylene-polyamine compound such as hexamethylenetetramine and triethylenetriamine may be exemplified.

In order to form the microcapsules according to the present invention, minute liquid particles of the component(s) of the adhesive agent, which is (are) to be encapsulated are dispersed in an aqueous

liquid in which the aminoplast prepolymer, the water-soluble cationic urea resin and anionic surfactant have been dissolved, and in the thus prepared aqueous suspension, an acid catalyst, for instance, a carboxylic acid of a low molecular weight such as formic acid, acetic acid and citric acid, an inorganic acid such as hydrochloric acid, nitric acid and phosphoric acid or a salt of which the aqueous solution exhibits an acidity or an easily hydrolyzable salt such as aluminum sulfate, titanium oxychloride, magnesium chloride, ammonium chloride, ammonium nitrate, ammonium sulfate and ammonium acetate is added, and then, while causing a complex-coacervation by the water-soluble cationic urea resin and the anionic surfactant both of which have been dispersed in the aqueous dispersion of the aminoplast, the prepolymer and the water-soluble cationic urea resin are brought into polycondensation to form a hydrophobic membranous wall of a high molecular weight which completely covers each of the minute liquid particles of the components of the adhesive agent, which have been dispersed in the system, thus resulting in micro-encapsulation.

In the case where the above-mentioned modifier is added to the system during the polycondensation, the capsular membranous wall comprising the aminoplast treated with the modifier as has been explained is formed.

The amount of the modifier is 0.1 to 30% by weight, preferably 0.5 to 20% by weight to the prepolymer, the modifier is preferably added as an aqueous solution thereof at a concentration of 0.02 to 5% by weight.

In this connection, the water-soluble cationic urea resin used for taking place the complex coacervation and for preparing the above-mentioned aminoplast is the substance obtained by introducing a cationic modifying group into a urea-formaldehyde resin, namely the product of polycondensation of, for instance, urea-formaldehyde prepolymer with polyalkylenepolyamine, guanidine, diaminoethanol, dicyandiamide, diethylaminoethanol and quanylurea.

As the anionic surfactant, a substance such as those having a lipophilic group and an anionic hydrophilic group in their molecule, for instance, salts of fatty acid, sulfate esters of higher alcohols and salts of alkylarylsulfonate may be mentioned, and for instance, sodium dodecylbenzenesulfonate is preferably used.

In addition, in the polycondensation for the formation of the microcapsules in the present invention, it is important that the two kinds of substances which are mutually different from each other concerning their sign of electric charge are coexistent with the prepolymer, the one of the substances being the water-soluble cationic urea resin and the other of the substances being the anionic surfactant. Owing to such an important situation, it is possible to obtain a stabilized aqueous dispersion containing microcapsules uniform in quality.

Since the microcapsules of the present invention can be processed into a free-flowing powdery state after preparation by easily separating from the medium for dispersion used in the preparation thereof and drying thereof, the microcapsules are excellent in solvent-resistance, they are favorably suitable for forming the adhesive agent by uniformly dispersing in the other components of the adhesive agent.

The following is the concrete explanation of the adhesive agent containing the microcapsules according to the present invention (1) in the case where it is the type of chemical reaction and also (2) in the case where it is the type of solvent activation.

#### (1) Adhesive agent of the type of chemical reaction:

For the preparation of the adhesive agent of the type of chemical reaction, namely the adhesive agent comprising a resin, a monomer or oligomer for adhesion, an initiator of the reaction and a hardener, any one of these components may be encapsulated in the microcapsules and the microcapsules may be dispersed in a mixture of the other components. As the component encapsulated in the microcapsules, the component smaller in amount, namely the initiator of the reaction or the hardener is generally selected. The kinds of the components encapsulated in the microcapsules may be not less than two, and not less than two kinds of the components may be encapsulated together or the respective components may be separately encapsulated.

As the resin for adhesion, poly(acrylic acid), poly(methacrylic acid), epoxy resin, polyester, polyamide, polyurethane, copolymer of urethane and lower alkyl acrylate or lower alkyl methacrylate, copolymer of dicarboxylic acid, diol and lower alkyl acrylate or lower alkyl methacrylate, epoxidized poly(lower alkyl acrylate), epoxidized poly(lower alkyl methacrylate), low-molecular silicone resin, natural rubber, neoprene rubber, poly(vinyl acetate) and polystyrene may be mentioned. The microcapsules containing the necessary initiator for the reaction or the necessary hardener are dispersed in at least one resin selected from the above-mentioned resin and their monomers or oligomers for adhesion or in a solution prepared by dissolving thereof in an organic solvent.

As the initiator of the reaction, dibutyl-tin dilaurate, stannous caprylate or a solution of an organic peroxide such as benzyl peroxide and dibutyl peroxide in an organic solvent may be mentioned, and as the hardener, N,N-dimethylaniline, N,N-dimethyltoluidine and the like may be mentioned.

In the case of utilizing the adhesive agent containing microcapsules of the type of chemical reaction, it is painted on one of the surfaces of a body, which is to be adhered and then the other body

to be adhered to the first body is piled onto the first body, so as to pinch the thus painted surface of the first body and then a pressure is applied onto the thus piled bodies from the side of the second body.

Then the microcapsules are easily broken to allow the free contact of the content of the microcapsules with the other components painted on the surface of the first body thereby the hardening is proceeded to obtain a strong adhesion of the two bodies. The adhesive agent containing microcapsules of the type of chemical reaction can be applied to any surface by one of several means such as printing, spraying, brushing, etc.

## (2) Adhesive agent of the type of solvent activation:

For the preparation of the adhesive agent of the type of solvent activation, the microcapsules containing an organic solvent activating the resin which constitutes the adhesive membrane may be dispersed in the resin solution which constitutes the adhesive membrane.

As the organic solvent possibly encapsulated, almost all the generally used solvents are suitable for use, and hexane, heptane, benzene, toluene, xylene, carbon tetrachloride, trichloroethylene and tetrachloroethylene may be mentioned.

As the resin activated by the solvent, neoprene rubber, butyl rubber, styrene-butadiene rubber, natural rubber, polystyrene, poly(vinyl acetate), methylcellulose, ethylcellulose, poly(vinyl chloride), copolymer of ethylene and vinyl acetate, acrylic resin, methacrylic resin, polyamide, copolymer of vinyl acetate and lower alkyl acrylate may be mentioned.

The adhesive agent of the type of solvent activation according to the present invention comprising the above-mentioned microcapsules containing the solvent as the core substance dispersed in the resin solution which is to constitute the adhesive membrane and the resin. On the occasion of applying the adhesive agent of the type of solvent activation, the adhesive agent is painted on the surface to be adhered of one of the two bodies to be adhered, and after drying the thus painted adhesive agent, the body thus having a painted surface is placed on to the other of the two bodies to be adhered while applying a pressure onto the first body, thereby the microcapsules being broken by the pressure to allow the solvent freely activate the component of the resin in the painted surface resulting in a good adhesion.

Also the adhesive agent containing microcapsules of the type of solvent activation can be applied by printing, spraying, brushing, etc. onto the surface of a body, which is to be adhered to other body.

Since the microcapsule used in the present invention can be easily broken by applying a pressure of lower than 10 kg/cm<sup>2</sup>, the above-mentioned adhesion of two bodies by lamination and pressing is easily carried out.

Accordingly, the adhesive agent containing microcapsules according to the present invention has a merit of utilizing in a broad field of adhering.

The present invention will be more precisely explained while referring to Examples as follows.

However, the present invention is not restricted to Examples under-mentioned. From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of the present invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions.

## 40 Example 1

### 1-1: Preparation of two prepolymers

After adjusting the pH of 162 g of aqueous 37% solution of formaldehyde (hereinafter referred to as formalin) by the addition of aqueous 2% solution of sodium hydroxide to 9.0, it was mixed with 63 g of melamine, and the mixture was brought into reaction while stirring the mixture at 70°C. Just after confirming the complete dissolution of melamine in the reaction mixture, 225 g of water were added to the reaction mixture, and the mixture was stirred for 3 min to obtain an aqueous solution of a prepolymer of melamine-formaldehyde resin (hereinafter referred to as M4F prepolymer, M4F meaning that the molar ratio of melamine to formaldehyde is 1:4 in the prepolymer).

Separately, after adjusting the pH of 146 g of formalin by the addition of triethanol amine to 8.5, it was mixed with 60 g of urea, and the mixture was brought into reaction for 1 hour at 70°C to prepare an aqueous solution of a prepolymer of urea-formaldehyde resin (hereinafter referred to as U 1.8 F prepolymer).

### 1-2: Preparation of a cationic urea resin

After adjusting the pH of a mixture prepared by mixing 162 g of formalin and 60 g of urea and stirring the mixture to 8.8 by the addition of triethanolamine, the mixture was brought into reaction for 30 min while stirring the mixture at 70°C. Into 40 g of the reaction mixture, 24 g of water and 3 g of tetraethylenepentamine were added, and the pH of the mixture was adjusted to 3.0 by the addition of aqueous 15% hydrochloric acid solution while stirring the mixture at 70°C, and the reaction was carried out for 1 hour. Since the pH of the reaction mixture was reduced with the progress of the reaction, aqueous 10% solution of sodium hydroxide was added to the reaction mixture to adjust the pH thereof to 3.0, and the reaction was continued at a reduced temperature of 55°C. At the time when the viscosity of the reaction mixture became 200 cps, the reaction mixture was neutralized with the

addition of aqueous 10% solution of sodium hydroxide and 400 g of water were added to the neutralized mixture to obtain an aqueous solution of the water-soluble cationic urea resin.

### 1-3: Microcapsulation

5 A mixture consisting of 100 g of M4F prepolymer (refer to 1-1), 50 g of U 1.8 F prepolymer (refer to 1-1), 158 g of the aqueous solution of the water-soluble cationic urea resin (refer to 1-2), 62 g of water and 1 g of triethanolamine was adjusted to pH of 5.2 by the addition of aqueous 10% solution of citric acid, and by admixing the mixture with 3 g of aqueous 10% solution of Neopelex® (sodium dodecylbenzenesulfonate, made by Kao-Atlas Co., Japan) a solution named as A-liquid was obtained. 5

10 Into the thus prepared A-liquid, 200 ml of xylene were dispersed so that the mean diameter of the dispersed particles of xylene is 30 to 50 micrometers. The thus obtained aqueous dispersion was brought into reaction for one hour while gently stirring the dispersion and maintaining the dispersion at a temperature of 30°C and adding aqueous 10% solution of citric acid to the dispersion to adjust the pH of the dispersion at 3.6. After the lapse of further one hour, aqueous 10% solution of citric acid was added to the reaction mixture to adjust the pH thereof to 3.0, and then 20 ml of aqueous 10% solution 15 of resorcinol were added to the mixture. The microcapsulation was completed after the further continued stirring for 18 hours. After collecting the thus formed microcapsules, the capsules were washed with water and dried in an air-drier at 35°C to be powdery microcapsules of the mean diameter of 30 to 50 micrometers. 15

### 1-4: Preparation of an adhesive agent being the type of solvent activation as the final product

20 To a solution prepared by dissolving 100 parts by weight of masticated neoprene rubber in 500 parts by weight of toluene, one part by weight of a phenol resin and one part by weight of a coumaron resin were dissolved, and after adding 30 parts by weight of the microcapsules prepared in (1-3) to the thus prepared mixture, the whole mixture was uniformly mixed to obtain the adhesive agent containing the microcapsules. 20

### 25 Examples 2 to 9:

In the same procedures as in Example 1 except for using each prepolymer for membranous wall-formation and each modifier shown in Table 1 instead of those used in Example 1, eight kinds of the adhesive agents according to the present invention were obtained. 25

Table 1

Example no.	Prepolymer for forming membranous wall of microcapsule (g)	Weight percent of material for membrane in microcapsule	Modifier and its amount		Mean diameter of microcapsules (micrometers)
			Modifier (% in water)	Amount (ml)	
1	M4F/U 1.8 F (100/50)	23.8	10, resorcinol	20	30 to 50
2	M4F (200)	23.7	10, resorcinol	40	30 to 50
3	U 1.8 F (100)	23.9	10, resorcinol	10	30 to 50
4	M4F/Tu 1.8 F <sup>*1</sup> (100/50)	24.3	10, resorcinol	120	30 to 50
5	M4F/Tu 1.8 F/U 1.8 F (38/18/18)	15.1	10, resorcinol	200	50 to 70
6	M4F/Tu 1.8 F/U 1.8 F (38/18/18)	15.1	10, hexamethylenetetramine	30	50 to 70
7	MTu4F <sup>*2</sup> (170)	20.0	10, triethylenetetramine	20	30 to 50
8	MTu U5F <sup>*3</sup> (122)	25.0	10, catechol	25	10 to 30
9	MU4F <sup>*4</sup> (177)	25.0	10, resorcinol	150	10 to 30

Notes: for <sup>\*1</sup>, <sup>\*2</sup>, <sup>\*3</sup> and <sup>\*4</sup>, refer to the following description on the respective prepolymers.

The respective prepolymers specified in Table 1 were prepared as follows:

#### Preparation of the prepolymers

##### \*1: Tu 1.8 F used in Example 4

5 After adjusting the pH of 146 g of formalin to 8.5 by the addition of triethanolamine, the former was mixed with 76 g of thiourea, and the mixture was brought into reaction for one hour at 70°C to obtain an aqueous solution of the prepolymer of Tu 1.8 F (one mol of thiourea: 1.8 mols of formaldehyde) 5

##### \*2: MTu4F used in Example 7

10 After adjusting the pH of 324 g of formalin to 9.0 by the addition of aqueous 2% solution of sodium hydroxide, the former was mixed with 63 g of melamine and 38 g of thiourea, and the mixture was brought into reaction at 70°C, and just after confirming the complete dissolving of melamine and thiourea into the reaction mixture, 425 g of water were added to the reaction mixture, and the resultant liquid was cooled to room temperature as it was. 10

##### \*3: MTuU5F used in Example 8

15 After adjusting the pH of 405 g of formalin to 8.5 by the addition of triethanolamine, the former was mixed with 42 g of melamine, 25 g of thiourea and 20 g of urea, and the mixture was brought into reaction at 70°C for one hour, and the product was cooled to room temperature. 15

##### \*4: MU4F used in Example 9

20 After adjusting the pH of 324 g of formalin to 8.5 by the addition of triethanolamine, the former was mixed with 63 g of melamine and 30 g of urea, and the mixture was brought into reaction for 30 min at 70°C. After adding 225 g of water to the reaction mixture, the mixture was cooled to room temperature. 20

#### Test Example 1:

25 Each of the adhesive agents respectively prepared in Examples 1 to 9 was painted on a plate of poly(vinyl chloride) of 0.5 mm in thickness at a rate of 6 g of the adhesive agent/m<sup>2</sup> of the plate, and by drying the thus painted plate for 2 hours at 40°C, a painted surface without stickiness was obtained. 25

Then, another plate of poly(vinyl chloride) of 0.5 mm in thickness was piled onto the painted surface of the plate to have a laminate having two layers of poly(vinyl chloride) intervened by a layer of the adhesive agent, and the laminate was passed between the two pitch-rolls of a rolling pressure adjusted to 10 or 200 kg/cm<sup>2</sup> to obtain an adhered body. 30

After leaving the adhered body as it was in an ordinary room for 24 hours, the adhesion between the two plates was tested. 30

The results are shown in Table 2 wherein the test results on the adhered body prepared by the adhesive agents prepared in the following Comparative Examples 1 to 5 are also shown for comparison. 35

Table 2

Adhesive agent prepared in	Adhesion of the two plates adhered under a pressure of	
	10 kg/cm <sup>2</sup>	200 kg/cm <sup>2</sup>
Example 1	good	good
Example 2	good	good
Example 3	good	good
Example 4	good	good
Example 5	good	good
Example 6	good	good
Example 7	good	good
Example 8	good	good
Example 9	good	good
Comparative Example 1	poor	good
Comparative Example 2	poor	poor
Comparative Example 3	poor	poor
Comparative Example 4	poor	poor
Comparative Example 5	poor	poor

#### Note to Table 2

40 In Table 2, adhesion good means that the two plates were so firmly adhered together that any one of the two plates could not be moved in regard to the other of them by hands, and on the other 40



hand, adhesion poor means that one of the two plates could be separated easily from the other by hands or the two plates were not adhered together.

#### Comparative Example 1

By the same procedures as in Example 1 except for dispensing the addition of resorcinol as the modifier, an adhesive agent containing microcapsules was obtained.

#### Comparative Examples 2 to 4:

While using 100 g of M4F prepolymer prepared by the same procedures as in Example 1(1-1) and 50 g of U 1.8 F pre-polymer also prepared by the same procedures as in Example 1(1-1), however, using one of the third components shown in Table 3 instead of the water-soluble cationic urea resin and Neopelex® in Example 1, thereby obtaining a liquid corresponding to A-liquid in Example 1, 176 g of xylene were dispersed in the liquid under the same conditions as in Example 1. In the case where the pH of the thus formed aqueous dispersion became lower than 5.0, the pH of the liquid corresponding to A-liquid was adjusted to 5.0 by the addition of aqueous solution of sodium hydroxide. The aqueous dispersion was brought into reaction under the same conditions and according to the same procedures as in Example 1, however, without adding the aqueous 10% solution of resorcinol to obtain an aqueous dispersion of microcapsules. After collecting the microcapsules and washing thereof with water, the washed microcapsules were air-dried.

By using the thus prepared microcapsules, an adhesive agent containing the microcapsules was obtained in the same procedures as in Example 1.

**Table 3**  
Substance used as the third component instead of water-soluble cationic urea resin and Neopelex®

<i>In Comparative Example</i>	<i>Substance used as the third component</i>
2	nothing used
3	Screeptest® 520 (copolymer of styrene and maleic anhydride, made by Monsanto Co.) as an aqueous 5% solution thereof: 75 g
4	a reactive surfactant (disclosed in Japanese Patent Application Laying-Open No. 46-7313 (1971)): 20 g

#### Comparative Example 5:

After dispersing 176 g of xylene in 275 g of an aqueous 10% by weight solution of gelatin at 50°C as particles of 30 to 50 micrometers in the mean diameter thereof, aqueous 10% solution of gum arabic and 450 ml of water were added thereto while gently stirring thereof, and after adjusting the pH of the thus formed mixture to 4.4 by the addition of aqueous 10% solution of acetic acid and leaving the mixture as it was for 10 min, the mixture was cooled to 5°C and 36.5 ml of aqueous 25% solution of glutaric aldehyde was added thereto, and the mixture was stirred for one hour. After heating the mixture again to 50°C and continuing the stirring for 30 min, the mixture was cooled to room temperature to obtain a slurry of microcapsules. By using the dried, powdery microcapsules obtained by spray-drying the slurry of microcapsules, an adhesive agent containing the microcapsules was prepared in the same procedures as in Example 1.

It was found by examining the respective adhesive agents prepared in Comparative Examples 2 to 5 that the organic solvent originally encapsulated in the microcapsules had been evaporated off completely from the microcapsules without leaving anything.

#### Example 10:

By the same procedures as in Example 1 except for using 176 g of a 5% solution of triallyl cyanurate in xylene or 176 g of a 5% solution of tertiary butyl perbenzoate in diethyl phthalate instead of 176 g of xylene in Example 1, two kinds of the powdery microcapsules were prepared.

Separately, an adhesive agent was prepared by adding 0.5 part by weight of benzyl peroxide and 10 parts by weight of methyl methacrylate into a solution prepared by dissolving 40 parts by weight of a tripolymer of ethylene, propylene and 1,4-hexadiene into 360 parts by weight of toluene and bringing the mixture into reaction for 5 hours at 80°C.

An adhesive agent of the type of chemical reaction was prepared by blending 100 parts by weight of the thus obtained tri-polymer and 6.5 parts by weight of the powdery microcapsules prepared by using triallyl cyanurate and 4.0 parts by weight of the powdery microcapsules prepared by using Perbutyl Z. By painting the thus prepared adhesive agent on the two respective lauan plates and

laminating them with their painted surfaces together and pressing the thus laminated body under a pressure of 10 kg/cm<sup>2</sup> at 50°C, a favorably laminated and adhered body was obtained.

In addition, the thus prepared adhesive agent containing the two kinds of the microcapsules retained the original adhesion even after one month of preservation.

#### 5 Example 11:

By the same procedures as in Example 2 except for using 224 g of diethyl phthalate containing 5% by weight of benzyl peroxide instead of 176 g of xylene in Example 2, a kind of microcapsules was prepared.

10 Separately, a mixed solution was prepared by dissolving 7 parts by weight of poly(methyl methacrylate) in a mixed solvent consisting of 150 parts by weight of butyl acetate, 120 parts by weight of ethyl acetate and 30 parts by weight of methyl isobutyl ketone, and further adding 40 parts by weight of methyl methacrylate and 1.0 part by weight of N,N-dimethyl-p-toluidine to the thus formed solution.

By admixing the thus prepared mixed solution with 6.5 parts by weight of the microcapsules prepared as above, an adhesive agent, of the type of chemical reaction, was obtained.

15 After spraying the adhesive agent onto a soft steel plate and evaporating the solvent, another soft steel plate was placed on the thus painted surface of the former soft steel plate, and by applying a pressure of 10 kg/cm<sup>2</sup> onto the thus laminated soft steel plates, a laminated and adhered body of soft steel plate was obtained while breaking the microcapsules, and the body showed a strong adhesion between the components after 10 min.

#### Comparative Example 6:

In the same procedure of microcapsulation in Comparative Example 5 except for using 224 g of diethyl phthalate containing 5% by weight of benzyl peroxide instead of 176 g of xylene in Comparative Example 5, a kind of microcapsules was obtained.

25 After preparing an adhesive agent by admixing 6.5 parts by weight of the thus prepared microcapsules with the same mixed solution as in Example 11, the thus prepared adhesive agent was sprayed on a soft steel plate and evaporated the solvent. By placing another soft steel plate on the thus painted and dried surface of the former soft steel plate and applying a pressure of 10 kg/cm<sup>2</sup> onto the thus laminated soft steel plates as in Example 11, a laminate body was obtained, however, the adhesion between the two plates was not satisfactory. No improvement of adhesion was obtained in another test of soft steel plate lamination even by applying a pressure of 200 kg/cm<sup>2</sup> while using the same adhesive agent.

#### Example 12:

35 By the same procedures for preparing the microcapsules as in Example 6 except for using 180 g of a mixture of 100 parts by weight of Epon 828 (an epoxy-resin, made by du Pont Co.; "Epon" is a Registered Trade Mark) and 10 parts by weight of xylene instead of 176 g of xylene in Example 6, a slurry of microcapsules was prepared.

After collecting the microcapsules from the slurry, the microcapsules were washed with water and dried to be freely-flowing powdery microcapsules.

40 By admixing a solution prepared by dissolving 100 parts by weight of N-methoxy-(methacrylate-nylon), so-called nylon 8, into 200 parts by weight of methanol with 20 parts by weight of the thus prepared free-flowing powdery microcapsules, an adhesive agent containing microcapsules was prepared.

45 After painting the thus prepared adhesive agent on a single lauan plate, another single lauan plate was placed thereon and by applying a pressure of 10 kg/cm<sup>2</sup> onto the thus laminated body at 70°C, a strongly adhered body of laminated lauan plates was obtained.

Even after leaving the thus laminated body for one week at a temperature of 70°C and a relative humidity of 75%, no noticeable deterioration of adhesion was found between the adhered plates.

50 In addition, the thus prepared adhesive agent containing the microcapsules could be preserved in a stable state without gellifying even after one month.

#### Claims

1. An adhesive of the chemical reaction or solvent activation type, which adhesive comprises microcapsules consisting essentially of at least one of the components constituting the adhesive encapsulated within a membrane composed of an aminoplast treated by a modifier, the microcapsules being dispersed in a medium consisting essentially of the other or each component constituting the adhesive.

2. An adhesive according to claim 1, wherein said aminoplast is a polycondensate formed from at least one prepolymer selected from melamine-formaldehyde prepolymers, urea-formaldehyde prepolymers, melamine-urea-formaldehyde pre-polymers and melamine-thiourea-urea-formaldehyde prepolymers or at least one mixed prepolymer containing a melamine-formaldehyde prepolymer and a

thiourea-formaldehyde prepolymer, in the presence of a water-soluble cationic urea resin and an anionic surfactant.

3. An adhesive according to claim 1 or 2, wherein said modifier is a phenolic compound.

5 catechol, hydroquinone, cresol, xyleneol or saligenin. 5

5. An adhesive according to claim 1 or 2, wherein said modifier is a polyalkylenepolyamine.

6. An adhesive according to claim 5, wherein said polyalkylenepolyamine is hexamethylenetetramine or triethylenetetramine.

10 7. An adhesive of the chemical reaction type according to any one of the preceding claims, wherein said microcapsules encapsulate a reaction initiator and/or a hardener as said core substance. 10

8. An adhesive according to claim 7, wherein said reaction initiator is dibutyltin dilaurate, stannous caprylate, benzyl peroxide or dibutyl peroxide.

9. An adhesive according to claim 7 or 8, wherein said hardener is N,N-dimethylaniline or N,N-dimethyltoluidine.

15 10. An adhesive of the solvent activation type according to any one of claims 1 to 6, wherein said microcapsules encapsulate a solvent which activates a resin which constitutes the medium in which the microcapsules are dispersed. 15

11. An adhesive according to claim 10, wherein said solvent is benzene, toluene, xylene, hexane, heptane, carbon tetrachloride, trichloroethylene or tetrachloroethylene.

20 12. A process for preparing an adhesive as claimed in any one of the preceding claims which process comprises dispersing minute liquid particles of at least one of the components of the adhesive in an aqueous dispersion of the components for forming an aminoplast; adding an acid catalyst to said aqueous dispersion, thereby causing polycondensation of polymer of said components for forming said aminoplast; adding a modifier to said aqueous dispersion during said polycondensation, thereby forming the microcapsules; collecting and drying the thus formed microcapsules; and dispersing said microcapsules in the or each other component of the adhesive. 25

13. A process according to claim 12, wherein the modifier is added in an amount of from 0.1 to 30% by weight.

30 14. A process according to claim 13, wherein the modifier is added in an amount of from 0.5 to 20% by weight. 30

15. A process according to any one of claims 12 to 14, wherein the modifier is added as an aqueous solution containing 0.02 to 5% by weight thereof.

35 16. A process according to any one of claims 12 to 15, wherein said acid catalyst is formic acid, acetic acid, citric acid, hydrochloric acid, nitric acid, phosphoric acid, aluminum sulfate, titanium oxychloride, magnesium chloride, ammonium chloride, ammonium nitrate, ammonium sulfate or ammonium acetate. 35

40 17. A process according to any one of claims 12 to 16, wherein the aminoplast is a resin formed by polycondensation of at least one prepolymer selected from melamine-formaldehyde prepolymers, urea-formaldehyde prepolymers, melamine-ureaformaldehyde prepolymers and melamine-thiourea-urea-formaldehyde prepolymers, or at least one mixed prepolymer containing a melamine-formaldehyde prepolymer and a thiourea-formaldehyde prepolymer, in the presence of an anionic surfactant and a water-soluble cationic urea resin obtained by bringing a urea-formaldehyde prepolymer into polycondensation with a polyalkylenepolyamine, guanidine, diaminoethanol, dicyandiamide, diethylaminoethanol or guanylurea. 40

45 18. A process according to claim 17, wherein said anionic surfactant is a salt of a fatty acid, a sulfate ester of a higher alcohol or a salt of an alkylarylsulfonate. 45

19. An adhesive containing microcapsules substantially as hereinbefore described in any one of Examples 1 to 12.

50 20. A process for the preparation of an adhesive containing microcapsules, said process being substantially as hereinbefore described in any one of Examples 1 to 12. 50

21. A method for adhesively bonding two surfaces together, which method comprises applying to one of the surfaces an adhesive as claimed in any one of claims 1 to 11 or 19 or which has been produced by a process as claimed in any one of claims 12 to 18 or 20, and bringing the two surfaces together under pressure sufficient to cause the microcapsules in the adhesive to burst.

55 22. A method for adhesively bonding two surfaces together, said method being substantially as hereinbefore described in Test Example 1 with reference to any one of Examples 1 to 9 or in any one of Examples 10 to 12. 55

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